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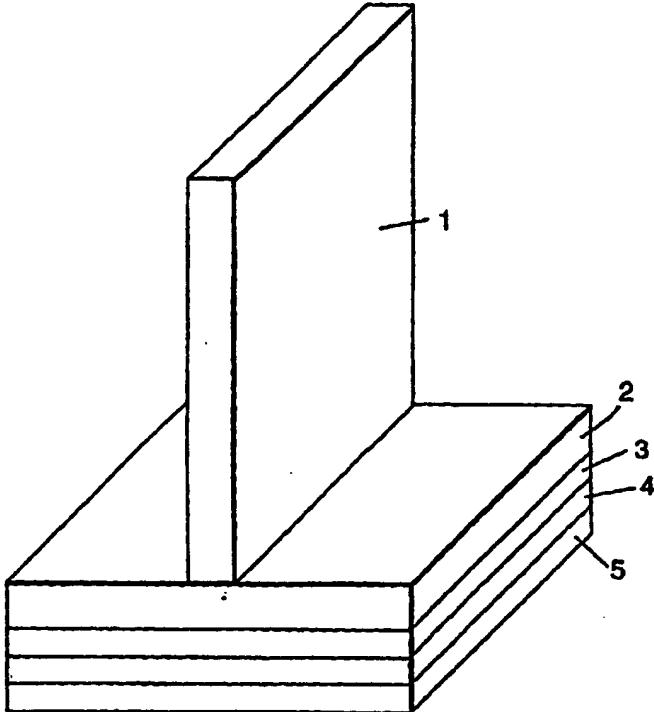
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## (57) Abstract

A self-adhesive film having no tackiness, which can repeatedly be used, and show no cohesive failure even if crosslinked films are adhered to each other and then debonded, and which can be prepared from a simple material is provided. A film composed of a copolymer of the monomer of an acrylic acid ester and the oligomer of a (meth)acrylic acid ester having a mutually reactive functional group in a molecule. The Tg value of a homopolymer obtained by homopolymerization of the aforesaid acrylic acid ester monomer is higher than 20 °C ( $T_g > 20$  °C). The Tg value of a homopolymer of the (meth)acrylic acid ester forming the aforesaid oligomer is lower than -20 °C ( $T_g < -20$  °C), and the F value defined by the following equation is within the range between  $2.8 \times 10^{-3}$  and  $3.7 \times 10^{-3}$ .  $F = W_1/(T_{g1} + 273.2) + W_2/(T_{g2} + 273.2) + \dots + W_n/(T_{gn} + 273.2)$ .  $W_1$  to  $W_n$  denote, respectively, the weight fraction of the first to n-th components, consisting of the monomer and the oligomer, and  $T_{g1}$  to  $T_{gn}$  denote, respectively, the Tg values (°C) of the first to n-th components, consisting of the homopolymer of the (meth)acrylic acid ester monomer and the oligomer.



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SELF-ADHESIVE FILM AND LAMINATE USING THE SAMEField of the Invention

5        The present invention relates to a self-adhesive film produced from a  
          (A) monomer of a (meth)acrylic acid ester and (B) an oligomer of a  
          (meth)acrylic acid ester. Component B has a reactive functional group(s)  
          capable of polymerizing with Component A. The self-adhesive film has  
          substantially no surface tackiness. The "self-adhesive film" herein referred to  
10      means a film-like adhesive capable of imparting a high adhesion strength by  
          being self-contacted and pressed.

Background Art

Hitherto, in order of fix objects to each other, retain an object or  
15      temporarily put a thing in position, adhesives, pressure-sensitive adhesives, and  
          self-fusion-bonding substances have been widely used. These substances have  
          generally strong surface tackiness, and exhibit adhesion function owing to this  
          surface tackiness. However, in these adhesives and the like, the cohesive force  
          has to be reduced in order to obtain high surface tackiness. As a result, it has  
20      been impossible to apply these adhesives and the like to a use in which an  
          object once adhered to itself is to be debonded i.e., reopened or restripped  
          (such as can be done with a hook-and-loop fastener) because the adhesive or the  
          like cause a cohesive failure. In addition, because of the surface tackiness, dust  
          and rubbish are liable to be adhered to the surface of these adhesives and the  
25      like, and the adhesion strength or the like greatly changed. Also for this  
          reason, these adhesives and the like have been unsuitable for applications in  
          which repeated openings and closings are desired.

In the following, the adhesives in the prior art will be discussed.  
Japanese Unexamined Patent Publication (Kokai) No. 2-102282 discloses a self-  
30      adhesive material formed by applying a pressure-sensitive adhesive onto a base  
          material. However, this pressure-sensitive adhesive is tacky. As a result, it is  
          liable to be contaminated by dust and the like sticking to it.

Japanese Unexamined Patent Publication (Kokai) No. 2-6578 discloses a self-fusion-bonding tape prepared by mixing uncrosslinked rubber and crosslinked rubber. However, when this tape is self-contacted and allowed to stand for a predetermined period of time, so as to be integrated, cohesive failure results when the adhered parts are debonded. It is, therefore, impossible to use the tape again. In addition, this tape requires a long period of time in order to obtain a sufficient adhesion strength.

Japanese Unexamined Patent Publication (Kokai) No. 1-138280 discloses a self-adhesive tape having an adhesive layer obtained by adding a tackifier to a styrene-ethylene-butylene-styrene copolymer. Although the coated surfaces of this self-adhesive tape are adhered under a slight pressure, this tape does not adhere to the surfaces of many other articles, even to a smooth surface such as that of stainless steel, even if a high pressure is applied. In addition, since this adhesive layer is of an uncrosslinked type, it dissolves when it comes into contact with a solvent. Furthermore, the adhesive layer is applied to a base material, from a solvent solution of the adhesive. This necessitates evaporation of the solvent after application. Consequently, the thickness of the adhesive layer cannot be made so large, and there is also caused a problem of environmental pollution.

Accordingly, for such use as mentioned above, there have been used only mechanical fasteners, e.g., "Velcro" (trade mark) hook-and-loop fastener available from the U.S.A. branch of Velcro Incorp., and mushroom type hook-and-loop fasteners such as "Scotch Mate" (trade mark) and "Dual Lock" (trade mark) available from 3M Company in U.S.A., and the like.

Thus, for solving the problems mentioned above, Japanese Patent Publication (Kokai) No. H3-191903 (corresponding to U.S. Pat. No. 5,196,266) discloses a specific high molecular weight material useable for restrippable fasteners. This high molecular weight material comprises at least one hard segment, at least one soft segment, a crosslinkable oligomer resin having a functional group, which is radiation functional addition-polymerizable, an ethylenically unsaturated monomer, and a photoinitiator. The photopolymer product of this composition has no surface tackiness. A high adhesion strength

can be obtained by contacting and pressing the parts of a same film. However, since a urethane compound is used for this product, it can exhibit poor weather (light) resistance and water resistance. Preferably, at least 3 components should be added. Accordingly, in this high molecular weight material, it has been  
 5 observed that homogeneous dispersion and mixing are comparatively difficult to achieve. When a homogeneous dispersion is not achieved, irregular adhesion strengths frequently result.

The present invention provides a self-adhesive film made of a simple and inexpensive material, which has little or no surface tackiness, which is  
 10 unlikely to be contaminated with dust and which causes no cohesive failure, even when parts of a same film are adhered to each other and thereafter debonded. The film of the invention is repeatedly usable. The present invention also provides an adhesive laminate prepared by use of such a self-adhesive film.

15

Summary of the Invention

The present invention provides a film having no or little surface tackiness. The film comprises a copolymer of (A) at least one (meth)acrylic acid ester monomer and (B) at least one (meth)acrylic acid ester oligomer.  
 20 Oligomer (B) contains a reactive functional group. Preferably, this group is a radiation polymerizable group.

The glass transition temperature of a homopolymer derived from monomer (A) has a  $T_g$  of greater than  $20^{\circ}\text{C}$ . The glass transition temperature of oligomer (B) is less than  $-20^{\circ}\text{C}$ . A film of the copolymer resulting from the  
 25 polymerization of monomer (A) and oligomer (B) preferably has a glass transition of from  $0$  to  $60^{\circ}\text{C}$ . When expressed in terms of the Fox equation, the copolymer film has an  $F$  value of from about  $2.8 \times 10^{-3}$  to  $3.7 \times 10^{-3}$ . The  $F$  value is calculated according to the following equation:

$$30 \quad F = \frac{W_1}{T_{g_1} + 273.2} + \frac{W_2}{T_{g_2} + 273.2} + \dots + \frac{W_n}{T_{g_n} + 273.2}$$

wherein  $W_1, W_2, \dots W_n$  denote the respective weight fractions of the first to the n-th components of monomer (A) and oligomer (B); and

5  $Tg, Tg_2 \dots Tg_n$  denote the respective glass transition temperatures (in °C) of each of the first to the n-th components of the polymer prepared from monomer (A) and oligomer (B).

10 The present invention provides a self-adhesive film which is not easily contaminated with dust and the like owing to the absence of tackiness. The film can repeatedly be used because no cohesive failure is caused even if the crosslinked films are adhered and then debonded. The film is excellent in 15 weather (light) resistance and water resistance, and can be prepared from a simple and inexpensive material.

15 **Brief Description of the Drawings**

Fig. 1 is a perspective view of a handle-bearing sample with the applied self-adhesive film of the invention as prepared in Example 1 hereinafter.

20 Fig. 2 is a graph showing the change of the self-adhesive strength (0 degree peel strength) of the self-adhesive film of the present invention as contrasted to the compositions of the oligomer and monomer of the present film.

25 Fig. 3 is a graph showing the change of the self-adhesion strength (0 degree peel strength) of the self-adhesive film of the present invention as contrasted to the thickness of the present film.

25

**Detailed Description**

30 Examples of useful (meth)acrylic acid ester monomers useful as monomer (A) materials include tert-butyl acrylate, isobornyl acrylate, dicyclopentenyl acrylate, 2-t-butylphenyl acrylate, 2-naphthyl acrylate, methoxyphenyl acrylate, n-hexadecyl acrylate, dicyclopentenyl acrylate, 2-methoxycarbonylphenyl acrylate, 2-ethoxycarbonylphenyl acrylate, 2-chlorophenyl acrylate, p-tolyl acrylate, methyl methacrylate, ethyl methacrylate,

n-butyl methacrylate, i-butyl methacrylate, t-butyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, glycidyl methacrylate, tetrahydrofurfuryl methacrylate, stearyl methacrylate, isobornyl methacrylate, dicyclopentanyl methacrylate, 2,2,3,3-tetrafluoropropyl methacrylate, 2,2,3,3,4,4-hexafluorobutyl methacrylate, perfluoroctylethyl methacrylate, dicyclopentenyl methacrylate, phenoxyethyl methacrylate, phenyl methacrylate, propyl methacrylate, i-propyl methacrylate, polyalkylene di(meth)acrylate ( $\text{CH}_2 = \text{CHCOO}(\text{CH}_2)_n \text{OCOCH} = \text{CH}_2$ ), polyoxyalkylene di(meth)acrylate ( $\text{CH}_2 = \text{CHCOO}((\text{CH}_2)_n \text{O})_m \text{COCH} = \text{CH}_2$ ), bisphenol A di(meth)acrylate, modified bisphenol A di(meth)acrylate, trimethylolpropane tri(meth)acrylate, modified trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, and the like.

Examples of (meth)acrylic acid ester monomers useful in preparing oligomer (B) include ethyl acrylate, n-butyl acrylate, i-butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, n-decyl acrylate, n-heptyl acrylate, n-hexyl acrylate, phenoxyethyl acrylate, propyl acrylate, i-octyl acrylate, isoamyl acrylate, butoxyethyl acrylate, methoxyethylene glycol acrylate, 2-methoxyethyl acrylate, 3-methoxypropyl acrylate, 3-methoxybutyl acrylate, 2-ethoxymethyl acrylate, 3-ethoxypropyl acrylate, isodecyl acrylate, lauryl methacrylate, n-octyl methacrylate, n-decyl methacrylate, n-dodecyl methacrylate, n-tridecyl methacrylate, n-undecyl methacrylate, and the like. Among these compounds, ethyl acrylate is preferable, because it is easily available and favorable for the F value to be within the aforesaid range.

The molecular weight of oligomer (B) is preferably within the range between 1000 and 20000. When this molecular weight is too low, the tack of the film of the present invention become too high. When this molecular weight is too high, the viscosity of the oligomer becomes so high that its handling becomes difficult.

Examples of the reactive functional group useful in the invention include a (meth)acryloyl group, an allyl group, a vinyl group, an epoxy group, and an hydroxyl group. When present in oligomer (B), the number of these is at

least 1 based on 10 or more, preferably 50 or more of the acrylic acid ester units in the oligomer, and preferably 1 based on 1000 or less, preferably 200 or less of the acrylic acid ester units of the oligomer. When the number of this functional groups is too small, the copolymer of the aforesaid monomer and 5 oligomer becomes paste-like, and does not form a film. On the other hand, when the number of the functional group is too many, self-adhesiveness is lost.

The Tg value of the homopolymer derived from monomer (A) is preferably 20°C or higher. When the Tg value of this homopolymer is lower than 20°C, the requirement cannot be satisfied that the self-adhesive film of the 10 present invention has no or little tackiness. On the other hand, the Tg value of oligomer (B) is preferably lower than -20°C. When the Tg value of oligomer (B) is -20°C or higher, the adhesiveness of the self-adhesive film of the present invention becomes insufficient and it becomes impossible to impart 15 flexibility to this film. Although it can be contrived to heighten the Tg value of oligomer (B) to a value higher than 20°C, and lower the Tg value of the homopolymer derived from monomer (A) to a value lower than -20°C, the obtained film has no self-adhesiveness.

The copolymer film of the invention may be prepared by exposing a mixture of monomer (A) and oligomer (B) to active energy radiation such as 20 ultraviolet light or electron beam radiation so as to polymerize and harden the mixture.

When the mixture is to be hardened by exposure to ultraviolet irradiation, it is preferable to include a photopolymerization initiator to the mixture. Examples of useful photopolymerization initiators include benzoin, 25 benzoin methyl ether, benzoin ethyl ether, benzoin-n-propyl ether, benzoin-n-butyl ether, benzyl, benzophenone, p-methylbenzophenone, diacetyl, eosin, thionine, Michler's ketone, acetophenone, 2-chlorothioxanthone, anthraquinone, chloroanthraquinone, 2-methylanthraquinone,  $\alpha$ -hydroxyisobutylphenone, p-isopropyl- $\alpha$ -hydroxyisobutylphenone,  $\alpha,\alpha'$ -dichloro-4-phenoxyacetophenone, 30 1-hydroxy-1-cyclohexylacetophenone, 2,2-dimethoxy-2phenylacetophenone, methylbenzoin formate, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropene, dichlorothioxanthone, diisopropylthioxanthone, phenyl disulfide-2-

nitrososfluorene, butyloin, anisoin ethyl ether, azobisisobutylonitrile, tetramethyl thiuram disulfide, and the like. These compounds can be used each independently, or in combination of 2 or more of them.

5 The photopolymerization initiator is used preferably in a proportional amount normally ranging from about 0.1 to about 5 parts by weight based on 100 parts by weight of the sum amount of monomer (A) and oligomer (B). In addition, in order to promote the cure reaction by use of the aforesaid photopolymerization initiator, a photopolymerization promotor can be combined with the initiator. Typical examples of the photopolymerization promotor, 10 include tertiary amines such as triethylamine, triethanolamine, and 2-dimethylaminoethanol; alkylphosphines such as triphenylphosphine; thiols such as  $\beta$ -thioglycol; and the like.

15 The ultraviolet light may be provided by, for example, a mercury lamp, a high pressure mercury lamp, a ultra high pressure mercury lamp, a xenon lamp, a carbon arc, a metal halide lamp, sunlight, etc. The atmosphere in which the mixture is irradiated is preferably air or inert gas. When the atmosphere is air, it is preferable to use a high pressure mercury lamp as an irradiation source. The irradiation intensity of ultraviolet rays is preferably within the range between 0.1 and 100 mW, and the dose thereof is preferably 20 within the range between 100 and 20,000 mJ/cm<sup>2</sup>.

25 Polymerization by exposure to electron beam irradiation may be accomplished by employing a Cockcroft type accelerator, Cockcroft-Walton type one, resonant transformer type one, transformer type one, insulating core transformer type one, dynamitron type one, linear filament type one, broad beam type one, area beam type one, cathode electron type one, high frequency type one, and the like. The accelerating voltage for the electron beam irradiation is preferably within the range between 100 and 500 kV, and the dose thereof is preferably within the range between 10 and 1000 kGy.

30 The aforesaid F value is within the range between  $2.8 \times 10^{-3}$  and  $3.7 \times 10^{-3}$ . When the F value is less than  $2.8 \times 10^{-3}$ , the adhesiveness is insufficient and this case is not preferable. On the contrary, when this value is

larger than  $3.7 \times 10^{-3}$ , the present self-adhesive film has tackiness, and therefore, this case is also not preferable.

The criterion as to whether or not there is tackiness referred to in the present invention is defined by finger tackiness. The films of the invention exhibit substantially no finger tackiness.

The thickness of the film of the present invention is preferably within the range between 20 and 5000  $\mu\text{m}$ . When the film is too thin, the self-adhesiveness become lowered. On the contrary, when the film is too thick, the film becomes difficult to cure. This film may have smooth surfaces.

Alternatively, it may employ uneven surfaces. When the film has such uneven surfaces it is preferred that they mate with each other. In this case, the height of the unevennesses is preferably within the range between 10 and 1000  $\mu\text{m}$ . When the height is less than 10  $\mu\text{m}$ , the adhesion strength is only minimally improved, and when the height exceeds 1000  $\mu\text{m}$ , it becomes difficult for parts of the film to be fitted to each other.

In addition, the self-adhesive film may be adhered to a substrate so as to be laminated. In this case, the utility value of the film is increased. The film adhered to many different substrates. These include plates, tapes or other molded products having any shape. The substrate may be made from plastic, glass, metal, and the like.

#### Examples

The following examples further illustrate the present invention. It is to be noted that the scope of the present invention is not restricted by these working examples. In the following examples, "parts" should be construed as "parts by weight" unless otherwise specified.

#### Example 1

##### (1) Synthesis of acrylic acid ester oligomer:

250 g of ethyl acrylate, 5.8 g of 2-hydroxyethyl acrylate, and 0.4 g of 1-octanethiol were subjected to reflux in 1 L of methyl ethyl ketone in a nitrogen gas flow (about 80°C). A solution obtained by dissolving 0.8 g of

azobisisobutyronitrile in methyl ethyl ketone was added dropwise to the reaction system, whereafter reflux under stirring was continued for 6 hours, so as to effect polymerization. Stopping the heating and the introduction of nitrogen, the obtained polymer was cooled to room temperature, whereafter 4.8 g of 5 pyridine were added and stirred. A solution obtained by dissolving 5.4 g of acrylic acid chloride in methyl ethyl ketone was then added dropwise to the mixture, and stirred for 3 hours. The produced white precipitate of pyridinium chloride was eliminated by suction filtration, and methyl ethyl ketone was eliminated under reduced pressure, whereby an oligomer containing an acryloyl 10 group was obtained.

(2) Preparation of a film by UV irradiation:

A mixture consisting of 50 parts of the ethyl acrylate oligomer (oligomer (B)) synthesized in step (1), 50 parts of isobornyl acrylate 15 (monomer (A)), and 1 part of a photoinitiator (produced by Merk Inc.; trade name: "Dilocure 1173" (hereinafter referred to as "D1173") was sandwiched between two parts of a poly(ethylene terephthalate) (PET) film with a thickness of 100  $\mu\text{m}$ . The thickness of the mixture was controlled to 300  $\mu\text{m}$  by use of a knife coater. The sandwiched mixture was cured by UV irradiation (UVL-N 20 high pressure mercury lamp produced by Ushio Co., Ltd.; integral intensity: 900  $\text{mJ/cm}^2$ , measured by "UV-350" produced by ORC Inc.), so that a polymer film was prepared.

(3) Determination of 0 degree peel strength:

25 A cyano acrylate type adhesive was coated on an acrylic plate with a thickness of 1 mm, and onto the thus coated adhesive, there was adhered the film prepared in (2), from which the PET film on one side of the film had been stripped off. From the thus prepared laminate sample, there was cut out a one cm square part, and a handle of acrylic plate with a thickness of 2 mm was 30 adhered to the cut out laminate sample, so as to prepare a sample equipped with a handle. See Fig. 1. Fig. 1 shows a test specimen which comprises handle 1 secured acrylic plate 2. A layer of cyanoacrylate adhesive 3 secures a section

of the self-adhesive film 4 to the plate 2. A PET film 5 covers the self-adhesive film 4. A second test identical specimen (now shown) is used to measure the 0 degree peel strength. In measuring the 0 degree peel strength the PET film 5 is removed from each of the test specimens. The self-adhesive films 4 were then mutually contacted to each other. A load of 500 g was applied to each of the test specimens for one minute after which these films were pulled in the direction perpendicular to the plane of the contacted surfaces by gripping the handles in the jaws of a "Tensilon 100". The force applied between these surfaces when they were debonded was reported as the 0 degree peel strength.

10 The 0 degree peel strength was found to be 8.7 kgf/cm<sup>2</sup> (average value of 5 measured results).

Examples 2 to 8

15 The same experiment as in Example 1 was conducted with the exception that various acrylic acid ester monomers were used as reactive diluents. The Tg values of a homopolymer derived from the monomers used as the reactive diluent, F values, whether or not there was tackiness, and 0 degree peeling strength (kgf/cm<sup>2</sup>) in these cases are set forth in Table 1. In addition, whether 20 or not there was tackiness, and the degree of tackiness were judged according to whether or not there was sticky feeling and the degree of stickiness when a naked self-adhesive film was touched with a hand.

Table 1

| Example No. | Reactive Diluent Monomers <sup>1)</sup> | Tg (°C) <sup>3)</sup> | F value               | Tackiness <sup>2)</sup> | 0 degree peel |
|-------------|---|-----------------------|-----------------------|-------------------------|---------------|
| 5           | 2 EHA                                   | -50                   | $4.26 \times 10^{-3}$ | yes                     | -             |
| 10          | 3 EA                                    | -24                   | $4.02 \times 10^{-3}$ | yes                     | 2.8           |
| 15          | 4 BzA                                   | 6                     | $3.80 \times 10^{-3}$ | yes                     | 2.3           |
| 20          | 5 tBa                                   | 43                    | $3.58 \times 10^{-3}$ | no                      | 7.4           |
| 25          | 6 IBA                                   | 94                    | $3.37 \times 10^{-3}$ | no                      | 8.7           |
| 30          | 7 DCPA                                  | 120                   | $3.28 \times 10^{-3}$ | no                      | 7.8           |
|             | 8 HDDA                                  | 120                   | $3.28 \times 10^{-3}$ | no                      | 2.8           |

1) EHA: 2-ethylhexyl acrylate

EA: ethyl acrylate

BzA: benzyl acrylate

tBA: t-butyl acrylate

DCPA: dicyclopentanyl acrylate

HDDA: 1,6-hexanediol diacrylate

2) yes: there is tackiness when touched with a finger  
no: there is no tackiness when touched with a finger

3) Tg value of the homopolymer derived from the reactive diluent monomer.

25

### Examples 9 to 19

The same experiments as in Example 1 were conducted, with the exception that the ethyl acrylate oligomer synthesized in Example 1(1) was used as an oligomer, DCPA as a reactive diluent, so as to vary the composition ratio. The composition was applied between two 50  $\mu$ m thick PET films and exposed to UV irradiation. In addition, whether or not there was tackiness was judged according to whether a naked self-adhesive film was sticky or not when it was touched with a hand. The results are set forth in Table 2.

Table 2

| Example No. | X/Y      | Tackiness | 0 degree peel |
|-------------|----------|-----------|---------------|
| 5           | 9 100/0  | yes       | 2.0           |
|             | 10 90/10 | yes       | 2.4           |
|             | 11 80/20 | yes       | 3.4           |
|             | 12 70/30 | no        | 4.3           |
|             | 13 60/40 | no        | 4.8           |
| 10          | 14 50/50 | no        | 5.1           |
|             | 15 40/60 | no        | 4.8           |
|             | 16 30/70 | no        | 3.9           |
|             | 17 20/80 | no        | 1.9           |
|             | 18 10/90 | no        | 0             |
| 15          | 19 100/0 | no        | 0             |

Note) oligomer/DCPA/D1173 = X/Y/l, (X + Y = 100)  
unit of 0 degree peel: kgf/cm<sup>2</sup>

20 The results of Table 2, which have been plotted on a graph, are set forth in Fig. 2. It can be seen from Table 2 that the 0 degree peeling strengths have a distribution having a peak value thereof at a certain composition ratio.

#### Examples 21 to 25

25 The 0 degree peel strengths (determined in the same way as in Example 1) when the thickness of the self-adhesive film was varied is set forth in Fig. 3 (film thickness: 25  $\mu\text{m}$  (Example 21), 50  $\mu\text{m}$  (Example 22), 100  $\mu\text{m}$  (Example 23), 200  $\mu\text{m}$  (Example 24), and 300  $\mu\text{m}$  (Example 25)). The composition used the ethyl acrylate oligomer synthesized in Example 1(1) as an oligomer, and IBA as a reactive diluent. It can be seen from Fig. 3 that before the film thickness reaches to about 200  $\mu\text{m}$ , the self-adhesion strength of the film increases as the film thickness is increased, and even if the film thickness is increased above this value, the self-adhesion strength is hardly changed.

Example 26

A mixture of 50 parts of the ethyl acrylate oligomer synthesized in Example 1 (1) and 50 parts of isobornyl acrylate was sandwiched between two parts of a PET film with a thickness of 100  $\mu\text{m}$ , and the whole film thickness 5 was controlled by use of a knife coater, so as to become 300  $\mu\text{m}$ , following which the sandwiched mixture was cured by electron beam irradiation (EB accelerator: an area beam type electron beam irradiator produced by Nissin High Voltage Co., Ltd.; in a nitrogen atmosphere, at an accelerating voltage of 300 kV, at an electron current of 30 mA, and at a dose of 100 kGy), whereby a 10 film was prepared. In the same way as in Example 1, there was prepared a sample with a handle, and 0 degree peel strength was determined. The measured value was found to be 5.5 kgf/cm<sup>2</sup>.

Example 27

15 A test sample with a handle was prepared as described in Example 1. The PET film was removed and the sample allowed to stand indoors for a week. The 0 degree peel strength was then determined. The 0 degree peel strength was found to be 8.6 kgf/cm<sup>2</sup>. This value is almost equal to the result obtained in Example 1, which shows that the self-adhesive film of the present 20 invention is hard to be influenced by dust and the like.

Example 28

Test samples, each with a handle, were prepared as described in Example 1. The self-adhesive film surfaces were then adhered to each other 25 according to the method in Example 1, and were then once debonded. These film surfaces were then again adhered in the same way as above, and 0 degree peel strength of the sample was determined and found to be 8.6 kgf/cm<sup>2</sup>. This value is almost equal to the result obtained in Example 1, which shows that the self-adhesive film of the present invention can repeatedly used.

**CLAIMS:**

1. A self-adhesive film having a substantially no surface tackiness, comprising a copolymer of (A) at least one monomer of (meth)acrylic acid esters and (B) at least one oligomer of (meth)acrylic acid esters having at least one mutually reactive functional group in a molecule, in which the Tg value (glass transition point) of a homopolymer derived from monomer (A) exceeds 20°C and the value of Tg of oligomer (B) is lower than -20°C, and the F value of the copolymer, defined by the following equation, is within the range 5 between  $2.8 \times 10^{-3}$  and  $3.7 \times 10^{-3}$ .

$$F = W_1/(Tg_1 + 273.2) + W_2/(Tg_2 + 273.2) + \dots + W_n/(Tg_n + 273.2)$$

15 wherein  $W_1$  to  $W_n$  denote, respectively, the weight fraction of the first to n-th components, respectively, consisting of the homopolymer of monomer (A) and the oligomer, and  $Tg_1$  to  $Tg_n$  denote, respectively, the Tg values (°C) of the first to n-th components, respectively, consisting of the monomer and the oligomer.

20 2. A self-adhesive film according to claim 1 wherein the number-average molecular weight of the oligomer of the aforesaid (meth)acrylic acid ester is within the range between 1,000 and 20,000.

25 3. A self-adhesive film according to claim 1 wherein the aforesaid oligomer of the (meth)acrylic acid ester is a one formed from ethyl acrylate.

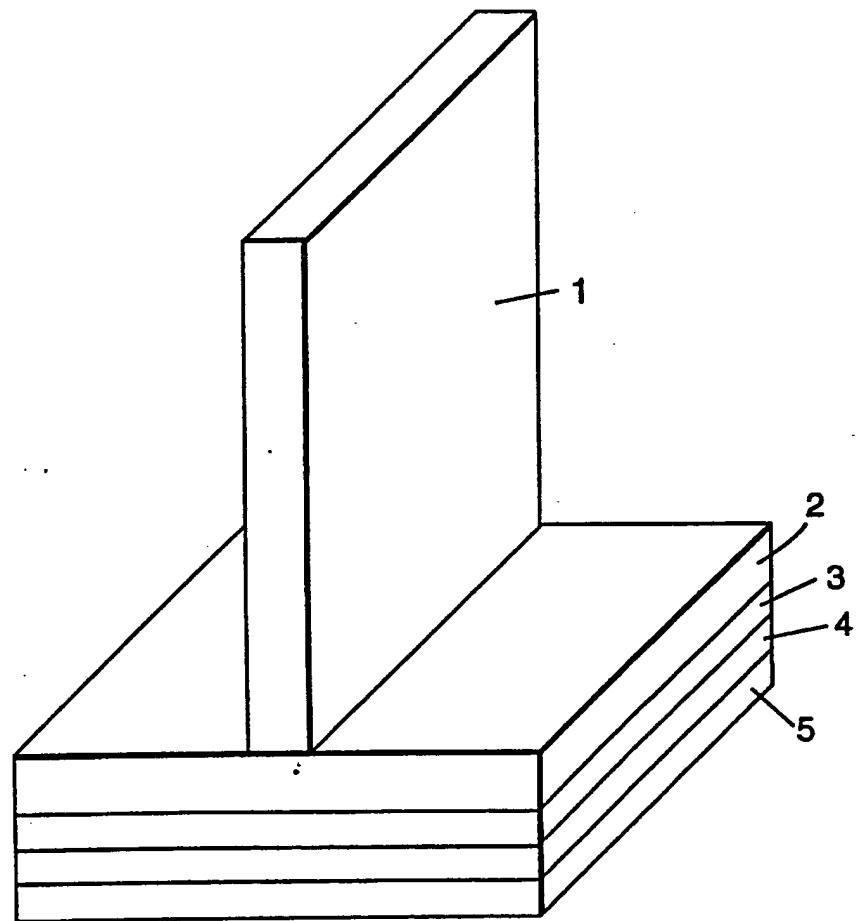
4. A self-adhesive film according to claim 1 wherein the thickness of the aforesaid film is within the range between 20 to 5,000  $\mu\text{m}$ .

30 5. A self-adhesive film according to claim 1 wherein there is unevenness in the height of the surface of the film ranging from 10 to 1,000  $\mu\text{m}$  of the surface.

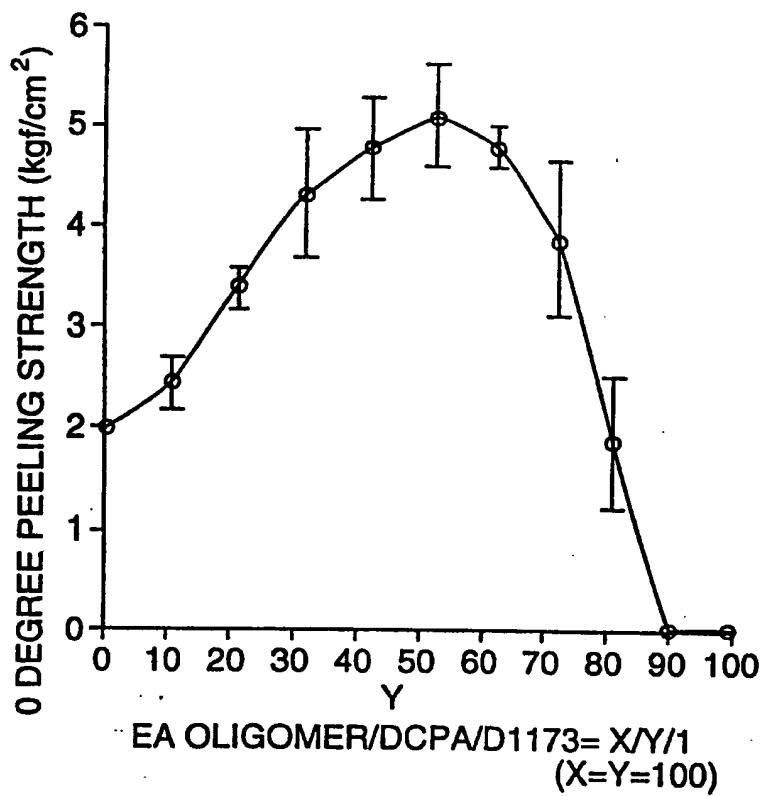
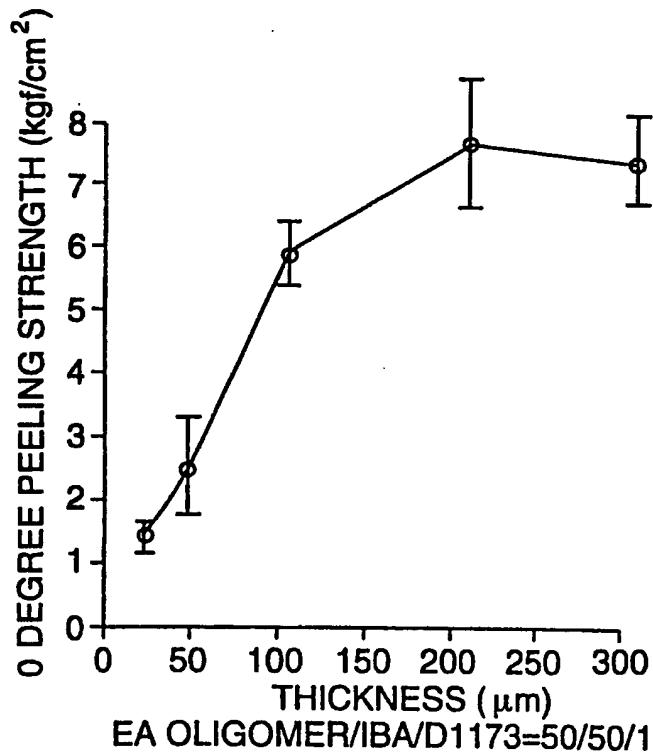
6. A laminate, in which the self-adhesive film of claim 1 is laminated on a substrate.

7. A self-adhesive film according to claim 1 wherein the copolymer is obtained by electron radiation polymerization of monomer (A) and oligomer (B), or by photopolymerization of monomer (A) and oligomer (B) by addition of a photopolymerization initiator in an amount ranging from 0.1 to 5 parts by weight based on 100 parts by weight of the sum amount of monomer (A) and oligomer (B).

10



***FIG.1***

**FIG.2****FIG.3**

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 94/08166

## A. CLASSIFICATION OF SUBJECT MATTER

C 09 J 133/06, C 09 J 7/00

According to International Patent Classification (IPC) or to both national classification and IPC 6

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 09 J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| A          | EP, A, 0 491 169<br>(LINTEC CORPORATION)<br>24 June 1992 (24.06.92),<br>claims.<br>--   | 1                     |
| A          | DERWENT ACCESSION<br>no. 89-361 125, Questel<br>Telesystems (WPIL),<br>DERWENT PUBLICATIONS LTD.,<br>London;<br>& JP,A,01 271 408<br>(SHIN-NAKAMURA KAGAK),<br>abstract.<br>----- | 1                     |

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

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Date of the actual completion of the international search

11 November 1994

Date of mailing of the international search report

13.12.94

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**ANHANG**

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

**ANNEX**

to the International Search Report to the International Patent Application No.

**ANNEXE**

au rapport de recherche international relatif à la demande de brevet international n°

PCT/US 94/08166 SAE 94910

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unter-richtung und erfolgen ohne Gewähr.

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|---|---|---|---|
| EP A2 491169  | 24-06-92  | EP A3 491169<br>JP A2 4216886<br>US A 5252395   | 05-08-92<br>06-08-92<br>12-10-93                                      |

